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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Production of Titanium Dioxide

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A PROCESS FOR THE PRODUCTION OF TITANIUM DIOXIDE

Abstract of the Disclosure

A process for the production of titanium dioxide by the sulfate process in which the liquid accumulating during washing of the titanyl sulfate hydrolysis hydrolyzate is fractionated and the dilute fractions are returned to the process while the relatively concentrated thin acid is fed to a waste disposal.

A PROCESS FOR THE PRODUCTION OF TITANIUM DIOXIDE

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This invention relates to a process for the production of titanium dioxide by the sulfate process, in which the liquid accumulating during washing of the hydrolyzate is fractionated and the dilute fractions are returned to the process while the relatively concentrated waste acid is fed to a recycling process.

It is known that, apart from raw material and process costs, the economy of titanium dioxide production is being increasingly influenced by the costs involved in treatment of the waste acid and by government-imposed wastewater levies. Accordingly, various processes have already been proposed with a view to reducing treatment costs by increasing the concentration of the waste acid or by directly recycling waste acid to the process. According to US 4,502,976, a waste acid of high concentration is separated from dilute washing acid through careful monitoring of the sulfuric acid concentration in the liquid accumulating during washing of the hydrolyzate. This dilute washing acid may advantageously be concentrated, optionally in part, by waste heat in a first evaporation stage.

According to DE-C 2,729,755, ilmenite is digested with a mixture of 62 to 75% sulfuric acid, recovered by concentration of waste acid by evaporation and separation of the metal sulfates, and at least 95% pure sulfuric acid and the digestion cake is dissolved with water and part of the waste acid formed during the

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Le A 26 808

5 hydrolysis of titanyl sulfate. However, this process is specially designed for the use of ilmenite as raw material, in addition to which narrow limits are imposed by the metal sulfates, particularly chromium sulfate, recycled with the waste acid.

10 Another major disadvantage of this process is that the  $\text{TiO}_2$  production process is seriously impaired by the very high proportion of waste acid (20 to 30%) used to dissolve the digestion cake. If the quantity of sulfuric acid used to digest the raw material is correspondingly reduced, a lower yield of  $\text{TiOSO}_4$  is obtained when the  
15 autothermal discontinuous digestion reaction is carried out on an industrial scale. If, on the other hand, the  $\text{H}_2\text{SO}_4:\text{TiO}_2$  ratio is kept constant during the digestion reaction, such a high  $\text{H}_2\text{SO}_4:\text{TiO}_2$  ratio is obtained in  
20 the titanyl sulfate solution through the waste acid used to dissolve the digestion cake that the hydrolysis yield and the  $\text{TiO}_2$  pigment properties are adversely affected.

Accordingly, the problem addressed by the present invention was to provide a process by which it would be possible, both with ilmenite and with titanium slag as  
25 raw material, to obtain a maximal proportion of the sulfuric acid used to digest the titanium raw material as highly concentrated waste acid from the process, thereby minimizing both treatment costs and wastewater pollution, without adversely affecting the process as  
30 a whole or the quality of the titanium dioxide pigment.

The present invention relates to a process for the production of titanium dioxide by digestion of titanium raw materials with sulfuric acid, dissolution of the

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5 digested material to form a titanyl sulfate solution,  
hydrolysis of the titanyl sulfate, separation of the  
hydrolyzate from the metal-sulfate-containing sulfuric  
acid, the so-called waste acid, washing of the hydroly-  
zate and calcination to the  $\text{TiO}_2$  pigment, the solution  
10 accumulating during separation of the solids from the  
suspension formed during hydrolysis of the titanyl sul-  
fate being fed entirely as waste acid to a treatment or  
recycling process and the liquid accumulating during  
washing of the hydrolyzate being divided into three or  
15 four fractions of decreasing sulfuric acid concentra-  
tion, the first fraction A accumulating being combined  
with the waste acid and fed to the treatment or re-  
cycling process, the second fraction B accumulating  
thereafter being used instead of water in the hydrolysis  
of the titanyl sulfate, the third fraction C being used  
20 to dissolve the digested material formed during di-  
gestion of the titanium raw material and, optionally,  
a fourth fraction D being used instead of water to wash  
the hydrolyzate or being removed as wastewater.

25 In a particularly preferred embodiment of the pro-  
cess, the waste acid fed to the treatment or recycling  
process has a concentration of at least 23% by weight  
 $\text{H}_2\text{SO}_4$  and preferably of at least 24% by weight  $\text{H}_2\text{SO}_4$

The fraction B returned to hydrolysis of the titanyl  
sulfate from washing of the hydrolyzate preferably contains  
30 7 to 23% by weight  $\text{H}_2\text{SO}_4$  and the fraction C used to dissolve  
the digested material 0.2 to 7% by weight  $\text{H}_2\text{SO}_4$ .

In one preferred embodiment of the process, hydrolysis  
of the titanyl sulfate is carried out using separately

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5 produced hydrolysis nuclei and fraction B is only added  
after at least 50% of the total duration of the hydrolysis  
process has elapsed.

10 Accordingly, the liquid accumulating during washing of  
the hydrolyzate is divided up into three or, optionally,  
four fractions according to the sulfuric acid concentra-  
tion. These fractions are then specifically returned to  
the process or are removed.

More particularly, the process comprises the following  
steps:

15 Titanium raw materials, particularly ilmenite or  
titanium slag, are digested in known manner with 80 to 95%  
sulfuric acid. The sulfuric acid used is preferably a  
mixture of at least 95% sulfuric acid or oleum and at least  
60% sulfuric acid recovered by concentration of waste  
20 acid from the sulfate process by evaporation and sepa-  
ration of the metal sulfates from the sulfuric acid.  
Alternatively, sulfuric acid recovered from waste acid  
by other recycling processes may also be used.

25 According to the invention, the preferably solid  
digested material which accumulates during digestion of the  
raw material is dissolved with the third fraction C of the  
solution accumulating during washing of the hydrolyzate.  
The fraction in question has an  $H_2SO_4$  content of 0.2 to 7%  
by weight. Water or other solutions containing sulfuric  
acid may be used together with fraction C.

30 The low concentration of fraction C rules out any  
adverse effect on the subsequent hydrolysis process or on  
the pigment quality.

35 Solids and, optionally, iron sulfate heptahydrate are  
separated off in known manner from the titanyl sulfate  
solution obtained.

5        Subsequent hydrolysis of the titanyl sulfate is  
carried out, for example, using separately produced  
hydrolysis nuclei, fraction B accumulating during  
washing of the hydrolyzate being added to the solution.  
Fraction B is preferably added after at least 50% of the  
total duration of the hydrolysis process has elapsed.  
10      The quantity of fraction B is gauged in such a way that  
the suspension contains 160 to 200 g (TiO<sub>2</sub>/l at the end  
of the hydrolysis process. The addition of fraction B  
containing 7 to 23% by weight H<sub>2</sub>SO<sub>4</sub> in accordance with  
the invention does not adversely affect pigment quality.  
15      However, the concentration of the waste acid is  
distinctly increased in relation to the concentration  
obtained where water is added in accordance with the  
prior art.

20        The hydrolyzate is separated, optionally by filtra-  
tion, from the mother liquor, the waste acid containing  
H<sub>2</sub>SO<sub>4</sub> and metal sulfates, and subsequently washed with  
water. The concentration of H<sub>2</sub>SO<sub>4</sub> and metal sulfates of  
the solution, which accumulates during this washing of  
the hydrolyzate, changes characteristically during the  
25      washing process. Initially, waste acid is displaced from  
the hydrolyzate by the washing water. The sulfuric acid  
concentration then falls slowly from the range of 24-27%  
by weight to values of 18 to 23% by weight. According  
to the invention, this concentrated solution is fed as  
30      the first fraction A to the waste acid until the H<sub>2</sub>SO<sub>4</sub>  
concentration of the solution flowing off has fallen to  
a value in the range of 24-15% by weight. The waste acid  
thus obtained contains 85 to 97% of the sulfate ions

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5 contained in the titanyl sulfate solution after separation of iron sulfate heptahydrate, corresponding to 80-93% of the sulfuric acid present in the suspension after hydrolysis of the titanyl sulfate. A fraction B is then separated off while the  $H_2SO_4$  concentration falls rapidly from 25-15 to 12-3% by weight. According to the  
10 invention, this fraction B with an average  $H_2SO_4$  content of 10-23% by weight contains 4-12% of the sulfuric acid present after hydrolysis and, as described above, is added during hydrolysis of the titanyl sulfate. The relatively highly dilute solution accumulating after the  
15 steep fall in concentration to less than 12% by weight  $H_2SO_4$  is separated as the third fraction C. According to the invention, this fraction C with, on average, 0.2-7% by weight  $H_2SO_4$  contains 1 to 5% of the sulfuric acid present after hydrolysis and is used to dissolve the  
20 digested material. A highly dilute fourth fraction D is optionally used instead of water to wash the hydrolyzate or is removed as wastewater. According to the invention, it contains less than 5% and preferably less than 1% of the sulfuric acid present after hydrolysis.

25 Whereas, according to DE-C-2 729 755, it is only possible to obtain a waste acid concentration of 21-23% by weight  $H_2SO_4$  and problems can be expected from the metal ions relevant to color of the pigment, particularly Cr or V ions, present in the recycled solutions, it  
30 has surprisingly been found that neither the titanium dioxide production process itself nor the quality of the pigment obtained is adversely affected by application of the process according to the invention. A major

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5 advantage of the invention is that it gives a waste acid  
of high concentration both where ilmenite and where  
titanium slag is used as the raw material and, at the  
same time, minimizes wastewater pollution. The waste  
acid concentration obtained, which is at least 23% by  
weight  $H_2SO_4$  and preferably 24-27% by weight  $H_2SO_4$ ,  
10 enables the cost of treatment by recycling to be  
distinctly reduced compared with the prior art.

The advantages of the process according to the  
invention are illustrated by the following Examples.

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#### Example 1

1,170 kg titanium slag containing 75% by weight  $TiO_2$   
and 405 kg ilmenite containing 54% by weight  $TiO_2$  were  
20 digested with 1,996 kg 77.2% sulfuric acid and 970 kg 27%  
oleum. (The 77.2% sulfuric acid had been recovered from  
waste acid in accordance with US 4,502,976. It contained  
5.8% by weight metal sulfates, including 345 ppm Cr in the  
form of chromium sulfate and 36 ppm V in the form of  
25 vanadium sulfate). The solid reaction product formed  
during the digestion reaction was dissolved with 3.4 m<sup>3</sup> of  
the fraction C separated off during the washing of the  
hydrolyzate of a preceding batch and 0.9 m<sup>3</sup> wash solution  
from the washing of the digestion residues. The solution  
30 was filtered and the titanyl sulfate hydrolyzed.

Hydrolysis was carried out as follows:

49 l of a suspension of hydrolysis nuclei separately  
produced by precipitation of titanyl sulfate with sodium  
hydroxide were added to 4.35 m<sup>3</sup> titanyl sulfate solution  
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(corresponding to 1 t  $\text{TiO}_2$ ). The mixture was brought to the boiling temperature by introduction of steam and boiled to the "match point". The introduction of steam was then interrupted for 30 minutes, after which more steam was introduced and the mixture boiled for 2.5 h. After a total process time of 2.5 h, 0.9 m<sup>3</sup> solution which had been separated as fraction B during washing of the hydrolyzate was added. 70 minutes after addition of the solution, the introduction of steam was stopped. The hydrolysis yield was 95.4%.

The suspension obtained was filtered, waste acid containing 26.9% by weight  $\text{H}_2\text{SO}_4$  accumulating as filtrate. The filter cake was then washed with water. The solution accumulating as filtrate during washing of the filter cake was divided into 4 fractions:

At the beginning of the washing process, the concentration of the solution fell slowly from 26.4 to 22-23% by weight  $\text{H}_2\text{SO}_4$  and then rapidly to values below 5% by weight. The first 2.9 m<sup>3</sup> filtrate were separated off as fraction A until a concentration of 23% by weight  $\text{H}_2\text{SO}_4$  had been reached. This fraction had an average concentration of 24.6% by weight  $\text{H}_2\text{SO}_4$  and was combined with the waste acid which had accumulated during filtration of the hydrolyzate suspension. The waste acid fed to the recycling process had an average concentration of 25.5% by weight  $\text{H}_2\text{SO}_4$ , 345 ppm Cr and 580 ppm V. It contained 95.2% of the sulfate ions used during digestion of the raw material. 0.9 m<sup>3</sup> of the filtrate were then separated off as fraction B while the concentration of the filtrate fell from 23 to 10.2% by weight  $\text{H}_2\text{SO}_4$ . The fraction B had an average concentration of 19.6% by weight  $\text{H}_2\text{SO}_4$ , 265 ppm Cr and 446 ppm V. It contained 9.3% of the sulfuric acid which was present in the suspension after hydrolysis. 2.4 m<sup>3</sup> solution were then separated off as fraction C. This filtrate fraction had a concentration of 5.5% by weight  $\text{H}_2\text{SO}_4$ , 19 ppm Cr and 32 ppm

V. It contained 5.4% of the sulfuric acid present on completion of hydrolysis.

When the filtrate stream was switched over as fraction D to the wastewater channel, the filtrate contained 3.1% by weight  $H_2SO_4$ . The concentration fell to 0.3% by weight  $H_2SO_4$ . 1.8% by weight of the sulfate ions used in the digestion of the raw material were removed.

The filter cake obtained after washing of the hydrolyzate was bleached by the addition of Al powder and sulfuric acid. The standardizing chemicals phosphoric acid, alkalis and rutile nuclei were then added to the filter cake, followed by calcination under standard conditions at  $950^\circ C$  in a rotary kiln to form rutile pigment.

The pigment thus obtained was substantially identical with the typical standard of normal production where water rather than fraction B was added during hydrolysis and the digested material was dissolved with water.

#### Example 2

In the digestion of the raw material, the same ore mixture as in Example 1 was digested with 2,055 kg 77.2% recovered sulfuric acid and 1,000 kg oleum. The digestion cake was dissolved with  $3.3\text{ m}^3$  of the filtrate separated off as fraction C. The digestion yield was 0.3% higher than in Example 1.

Hydrolysis was carried out as in Example 1 with addition of  $0.9\text{ m}^3$  washing filtrate (fraction B). The hydrolysis yield was 95.7%. The suspension obtained was filtered. The waste acid accumulating had a concentration of 26.3% by weight  $H_2SO_4$ . The filter cake was then washed with water and the washing filtrate separated into three fractions. Fraction A was separated off up to a concentration of 20.5% by weight  $H_2SO_4$ . It had an average sulfuric acid content of 23.3% by weight and was combined with the waste acid which had previously accumulated. The waste acid

fed to the recycling process contained 24.7% by weight  $H_2SO_4$ , 334 ppm Cr and 562 ppm V. It contained 97% of the sulfate ions used in digestion of the raw material; the remaining 3% were chemically fixed to the titanium oxide hydrolyzate.

After fraction A, 0.9 m<sup>3</sup> filtrate were separated off as fraction B while the  $H_2SO_4$  concentration fell from 20.5 to 6% by weight. Fraction B contained on average 17.8% by weight  $H_2SO_4$ , corresponding to 9% of the total sulfuric acid present after hydrolysis.

3.3 m<sup>3</sup> filtrate having an  $H_2SO_4$  concentration between 6 and 0.4% by weight, average 1.7% by weight, were separated off as fraction C. It contained 2.5% of the sulfuric acid present on completion of hydrolysis.

The hydrolyzate was processed to rutile pigment as in Example 1. The pigment substantially corresponded to the production standard.

WHAT IS CLAIMED IS:

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1. A process for the production of titanium dioxide comprising digesting titanium raw materials with sulfuric acid, forming a titanyl sulfate solution by dissolution of the digested material, hydrolyzing the titanyl sulfate to form a suspension of hydrolyzate and metal-sulfate-containing sulfuric acid, the so-called waste acid, separating the hydrolyzate and waste acid, feeding the waste acid to a treatment or recycling process, washing the hydrolyzate and separating the washing liquid accumulating during the washing of the hydrolyzate into fractions of decreasing concentrations, and calcining the hydrolyzate to form  $TiO_2$  pigment wherein the first fraction (A) of the separated fractions of the washing liquid is combined with waste acid and fed to the treatment or recycling process, the second fraction (B) is used instead of water in titanyl sulfate hydrolyses and the third fraction (C) is used to dissolve digested material from digestion of titanium raw material.

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2. A process according to claim 1, wherein a fourth fraction D separated from the washing of the hydrolyzate is used instead of water to wash hydrolyzate or is removed as wastewater.

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3. A process according to claim 1, wherein 80 to 93% of the sulfuric acid present in the suspension after hydrolysis of the titanyl sulfate is fed as waste acid

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Le A 26 808

5 to the treatment or recycling process, 4 to 12% of the  
sulfuric acid is returned to hydrolysis of the titanyl  
sulfate and 1 to 5% of the sulfuric acid is used to  
dissolve the digested material.

10 4. A process according to claim 1, wherein 0.1  
to 5% of the sulfuric acid is used to wash the hydro-  
lyzate or is removed as waste water.

15 5. A process according to claim 1, wherein the  
waste acid fed to the treatment or recycling process has  
a concentration of at least 23% by weight  $H_2SO_4$ .

20 6. A process according to claim 5, wherein the  
waste acid fed to the treatment or recycling process has  
a concentration of at least 24% by weight  $H_2SO_4$ .

25 7. A process according to claim 1, wherein the  
fraction B from washing of the hydrolyzate returned to  
the hydrolysis of titanyl sulfate contains 7 to 23% by  
weight  $H_2SO_4$ .

8. A process according to claim 1, wherein the  
fraction C used to dissolve the digested material con-  
tains 0.2 to 7% by weight  $H_2SO_4$ .

30 9. A process according to claim 1, comprising  
carrying out the hydrolysis of titanyl sulfate using  
separately produced hydrolysis nuclei and adding  
fraction B after at least 50% of the total duration of  
the hydrolysis process has elapsed.

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Le A 26 808

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